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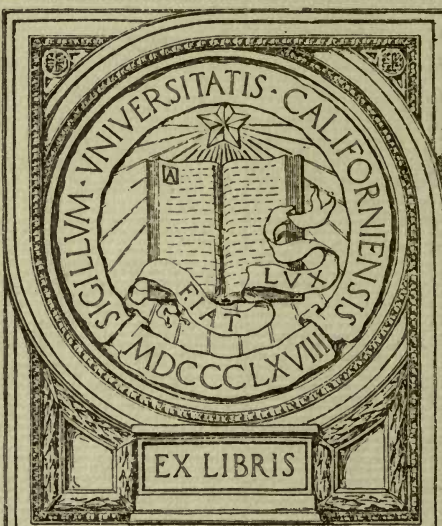
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The Catalytic Alkylation of Ammonia

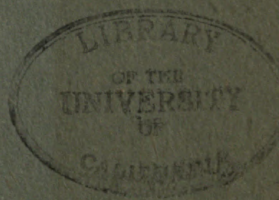
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JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

ARTHUR BENNETT BROWN



BALTIMORE
1922

UNIV. OF
CALIFORNIA

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ACKNOWLEDGEMENT

The author desires to take this opportunity to express his deep appreciation of the valuable advice and timely assistance of Dr. E. Emmet Reid, under whose direction this investigation was carried out.

He also wishes to acknowledge his indebtedness to Drs. Frazer, Lovelace, Patrick and Thornton for their truly generous instruction both in theory and in its practical application; and to Dr. C. H. Milligan, Grafflin Scholar of 1920-1921, for his many favors in the laboratory.

THE CATALYTIC ALKYLATION OF AMMONIA

BY ARTHUR BENNETT BROWN

Introduction

Sabatier and Mailhe¹ have shown that a mixture of primary, secondary and tertiary amines is formed by passing the vapor of an alcohol with ammonia over a variety of catalysts at elevated temperatures. Alumina, titania, zirconia, chromic oxide, the blue oxide of molybdenum, thoria, and the blue oxide of tungsten have been listed as catalysts, the last two mentioned being commonly regarded as the most efficient. While considerable qualitative data are available, the theoretical and practical importance of the reaction makes it advisable to secure more quantitative information than is now at hand. Hence the present investigation has for its purpose the quantitative study of the alkylation of ammonia by methyl, ethyl, n-propyl, and n-butyl alcohols, using various catalytic oxides at temperatures up to 500°C.

On account of the favorable reports that have been made of the activity of the blue oxide of tungsten in this reaction, much time was spent on it, the catalyst being prepared in a number of different ways in the hope of finding an active preparation but the yields of amines with it were all poor.

Thoria gave good yields of amines but also much aldehyde, the most of which passes into the nitrile.

Silica gel proved to be comparable to freshly prepared thoria in percentage conversion and much superior to thoria as well as alumina and zirconia in length of catalytic life and in freedom from destructive action on the alcohol not aminated. The peculiar thing about silica gel is the wide variation in its activity with seemingly slight variations in its preparation. A single sample of silica gel will give reproducible results, but two lots prepared in apparently the same way show different activity. A slow setting (6 to 9 hours) gel made from c.p. chemicals in exact proportions, thoroughly washed and slowly dried is apt to be an active catalyst. Silica gel impregnated with nickel oxide gave poor results; impregnated with thoria, fairly good. Commercial silica gel is a very poor catalyst for this reaction though in esterification it is almost as good as the specially prepared.²

Apparatus

The furnace used was the same as described by Kramer and Reid³ and the methods of operation similar. The anhydrous alcohol, accurately measured from a regulated dropper and calibrated tip, passed through a vertical tube

¹ Sabatier: *Catalysis in Organic Chemistry*, translated by Reid, p. 263, (1922); Sabatier and Mailhe: *Compt. rend.*, **143**, 1204 (1901); **148**, 898 (1909); **150**, 823 (1910); **153**, 160 (1911).

² Milligan and Reid: unpublished results.

³ J. Am. Chem. Soc. **43**, 880 (1921).

to the bottom of a 150 c.c. distilling bulb, immersed in an oil bath kept at 250°-300°, which served as a vaporizing and mixing chamber and preheater. Ammonia, from a cylinder, passed through a calibrated flowmeter and entered the mixing chamber through a side tube sealed into the vertical alcohol inlet tube. The reactants, passing from the side arm of the vaporization bulb, were led through an extension of the catalytic tube, where they were brought to the proper temperature by an electric preheating coil, and thence over the catalyst in the reaction tube, a pyrex tube (1.5-2 cm. $\times$ 45 cm.) uniformly heated in a horizontal electric furnace automatically regulated to within 1°, as read on a thermocouple laid beside the catalyst tube. The products of the reaction passed from the catalytic tube through a condenser into a collection bottle. A threeway stop-cock interposed permitted samples of the condensate to be taken without disconnecting the main receiver.

Analysis

After an extensive study of all the methods¹ that have been proposed for such mixtures we decided on the following plan, which is essentially that proposed by Weber and Wilson², though we did not come across their work until after our own was done. The method was tested out on known mixtures and the corrections thus found applied to the unknowns.

The reaction products were run for the desired time into standard sulphuric acid and titrated back with methyl red as indicator to determine total basic nitrogen. The solution was divided into aliquots, in one of which the total amine nitrogen was found by the method of François³ based on the selective precipitation of ammonia in presence of amines in a sodium hydroxide-carbonate solution by yellow mercuric oxide. The difference of these two represents the ammonia. In a second ammonia and primary amine are determined together by the method of van Slyke⁴ for the estimation of the amino group, the decomposition being effected at 90°. Tests with pure ammonium chloride and the hydrochloride of butyl amine prepared by the reduction of nitrobutane gave results 2% high—agreeing with van Slyke's observations on other amino compounds. Subtracting the previously determined ammonia from the van Slyke values gives the primary amine.

To estimate tertiary amine a third aliquot is placed in a 200 c.c. flask and sufficient sodium nitrite added to make a 25% solution. This is heated for an hour under reflux on a water bath, acetic acid being added from time to time to maintain slight acidity. A trap containing dilute sulphuric acid is connected with the top of the condenser to guard against loss of amine. After cooling, the solution is transferred to a Kjeldahl still, nitrogen oxides blown

¹ Heintz: *Ann.* **127**, 43 (1863); Hofmann: *Ber.* **3**, 776 (1870); Hinsberg: **23**, 2962 (1890); **33**, 3526-9 (1900); Hinsberg and Kessler: **38**, 906 (1905); Sudborough: *Proc. Roy. Soc.*, **20**, 165 (1904); *J. Chem. Soc.*, **95**, 447 (1909); Bertheanne: *Compt. rend.*, **150**, 1251-3 (1901); **151**, 146-9 (1911).

² *J. Biol. Chem.* **35**, 385 (1918).

³ *J. pharm. chim.* (6) **25**, 517 (1907); *Compt. rend.* **144**, 567-9 (1907) 857-9 (1907).

⁴ *Ber.* **43**, 3170 (1910).

off and strong alkali added, after which the tertiary amine is distilled into standard sulphuric acid and back titrated with methyl red as indicator. The secondary amine is estimated by difference from the above determinations.

The estimation of nitrile is effected by hydrolysis of an aliquot of the sample with 48% sulphuric acid in a pressure bottle at 100° for 1 hour. The product is diluted and steam distilled into 0.1 N. alkali and back titrated using phenolphthalein to determine the acid resulting from the hydrolysis of the nitrile.

Inasmuch as the amines are estimated through their nitrogen value, a complete analysis of a sample for primary, secondary, and tertiary amines is necessary for the determination of the percentage of alcohol converted into amines, since primary, secondary, and tertiary amines are equivalent as regards ammonia but stand in the ratios of 1:2:3 as to the alkyls used up. Consequently, two values for percentage alkylation will be met with in the following tables of experimental results: the one, used when only amine was estimated, termed simply "% amines" which gives the number of molecules of amines from 100 of alcohol, the other "% alkylation", used when complete analyses were made for primary, secondary, and tertiary amines. This value represents the amount of alcohol converted into amines. On the average this figure is 1.69 times the percent of amines, varying, of course, with the ratio of secondary and tertiary to primary, but remaining quite constant for butyl alcohol. In cases where complete analyses were not made, the percent of alcohol aminated can be approximated by multiplying the molecular percent by this factor. For the preliminary comparison of catalysts and for finding the optimum temperatures with various catalysts it is sufficient to consider the total amines formed as set down under "% amines".

Analysis of the gases was effected by collection of a timed sample in a Hempel burette over dilute sulphuric acid, adsorption of the ethylene hydrocarbon by fuming sulphuric acid, and determination of the residual hydrogen by explosion. The gas left after shaking with fuming sulphuric acid was always found to contain practically nothing but hydrogen.

A nitrile may be formed either from an aldehyde or from a primary amine with the liberation of 4 atoms hydrogen. We know little of the speed of the dehydrogenation of the primary amine but as relatively little of it is present during the passage of the mixture over the catalyst, it has been assumed, as a rough approximation, that all the nitrile was derived from the aldehyde, the amount of which can thus be calculated from the hydrogen found.

Experimental

Thoria Catalyst

In view of the efficiency of thoria as a dehydrating catalyst, this was the first catalytic substance employed. Catalyst A was prepared by pouring over enough shredded asbestos to fill the catalytic tube an almost saturated solution of thorium nitrate corresponding to 25 g. thoria, and evaporating to dryness in a vacuum desiccator over sulphuric acid. The resulting hard mass was shredded into small fragments, packed in the catalytic tube, and heated to

TABLE I—Catalyst A
Butyl Alcohol and Ammonia over Thoria—Asbestos.

Run	I	II	III	IV	V	VI	I
NH ₃ /BuOH Rate	1.5 6	2.4 9	1.6 3.1	1.15 8.9	1.5 6	1.5 6	1.5 6
Hrs. pre- vious use of catalyst	0	10	15	20	30	40	0
Temp.	Percent Amines Formed.						
36°	—	16.7	7.0	10.2	4.0	—	sec. — tert. — % Alkylation —
37°	25.3	—	7.6	12.7	3.6	—	— 5.5 40.2
38°	27.3	19.3	—	—	—	—	— 6.8 48.3
39°	28.0	21.3	8.1	14.6	5.1	8.9	— 4.5 46.0
41°	22.6	—	7.2	17.2	5.9	—	— 4.0 40.3
42°	—	16.8	—	12.9	6.3	—	— — —
43°	15.4	16.3	7.4	—	—	8.6	2.2 4.6 26.9

270°-300° in the furnace whereby the nitrate was converted to the oxide. After complete conversion, the catalyst was thoroughly scrubbed out with moist air at 400°C.

This catalyst was employed for the amination of butyl alcohol as shown in Table I. Some of the runs were at temperatures differing slightly from those given, but, as the temperature coefficient is not great, they have been grouped. The rate is time in hours required for the passage of one mole of the catalyst. For only the first run were the amines determined separately. The figures for these are given in the right hand portion of the table, together with the percent of alkylation.

The optimum temperature is 380°-390° for a fresh catalyst but rises to 420° or higher with prolonged use, the deterioration of the catalyst being more rapid during the first part of its life period. After having become coated with a carbonaceous deposit, the catalyst may be regenerated by treatment for several hours with moist oxides of nitrogen at 380°-400° followed by moist air, but does not recover its original activity, as is shown by run VI above. The regenerated catalyst is pure white but its surface is distinctly different—appearing grainy rather than powdery as it did originally.

Catalyst B likewise containing 25 g. thoria, was made in a similar manner with pumice as carrier.

This catalyst was tested with butyl alcohol at the rate of 1 mole in 5.8 hours with 1.3 equivalents of ammonia, with the following results:

TABLE II

Temp.	326°	342°	355°	369°	385°	396°
% Amines	1.64	3.65	4.18	6.65	8.55	10.2

The catalyst became darkened by a slight deposit but still appeared to be in good physical condition with a characteristic smooth surface.

Gas Evolution

Thoria has been rated by Sabatier¹ as a dehydration catalyst exclusively but Kramer and Reid² found only 2.7% of butylene to 32.7% of butyric aldehyde produced by their thoria catalyst at 380°, from which it appears that different preparations of thoria give widely different results. When ammonia is present the aldehyde formed is largely, but not completely converted, into nitrile with the evolution of a second molecule of hydrogen. Actually the furnace product gave, on distillation, a small fraction which smelled of aldehyde and gave the aldehyde test with fuchsin solution.

A run was made using the thoria-asbestos catalyst A with butyl alcohol vapor, 1 mole in 5.6 hours, and a slight excess of ammonia, the gas being collected and analyzed. If all of the alcohol had been converted to aldehyde 64.3 c.c. of hydrogen should have been formed per minute, if into nitrile, 128

¹ Sabatier: "Catalysis in Organic Chemistry." 233, (1922).

² J. Am. Chem. Soc. 43, 884 (1921).

c.c. and if into butylene, 64.3 c.c. of C_4H_8 . The results are given in Table III, the volumes given being cubic centimeters obtained per minute reduced to 0° and 760 mm.

TABLE III
Gases evolved from Butyl Alcohol and Ammonia

Temp.	Total Gas	C_4H_8	H_2	% Alcohol converted into C_4H_8	Nitrile
360°	10.3	1.17	8.97	1.82	7.04
374°	16.02	2.26	13.34	3.52	10.41
390°	29.87	4.02	23.90	6.25	18.6
405°	33.21	4.17	29.05	6.48	22.6
420°	57.28	8.04	49.25	12.5	38.3

The figures under "nitrile" were calculated on the assumption that all of the aldehyde formed had been converted into nitrile, that is by dividing the percentage of hydrogen by 2 which over-estimates the nitrile since some of the aldehyde remained as such. In a similar run using 1.45 mol. of ammonia to 1 of alcohol at the same rate, the nitrile was found to be 11.05 and 22.3% at 380° and 410° whereas calculated as above it would have been 12.8 and 29.5%. Calculating the aldehyde from the hydrogen remaining after subtracting that corresponding to the nitrile we have 3.5 and 14.4% of aldehyde remaining as such. Our thoria-asbestos was a poor catalyst for dehydrating butyl alcohol but excellent for producing aldehyde and nitrile by dehydrogenation. Above 400° a large proportion of the alcohol is used up in side reactions.

Tungstic Oxide Catalysts

Catalyst C. A tungstic acid hydrate gel¹ was made by the gradual addition of 6.38 N. nitric acid to a 12% solution of sodium tungstate, slowly until the first formed precipitates redissolves, then rapidly with vigorous stirring until the colorless solution takes on a clear yellow green color, the total acid required being 2.5 to 3.0 times the sodium tungstate equivalent. The gel after having set is thoroughly washed, and slowly dried at gradually increasing temperatures, and finally reduced at 300° with hydrogen to the blue oxide. Two runs were made using 78 g. of the reduced blue oxide gel.

Catalyst D. Unhydrated tungstic acid prepared by precipitation with hot concentrated hydrochloric acid from a hot solution containing 25 g. sodium tungstate, was thoroughly washed, and, in the form of a thin paste, was distributed over small fragments of pumice. This material was then slowly dried and reduced at 275° - 300° with ethyl alcohol vapor carried over it by air.

Catalyst E. Pumice in small fragments was impregnated with 25 g. tungstic acid dissolved in aqueous ethyl amine, dried, packed in the catalyst tube and heated to 300° in current of air. The trioxide was then reduced to

¹ Method worked out in this laboratory by Dr. C. H. Milligan to whom we are indebted for 32 g. of this gel.

the blue with alcohol vapor at 350° . The resulting catalyst was notable for its adherent qualities and even distribution of the blue oxide.

Catalyst F was prepared by suspending 40 g. of commercial blue oxide of tungsten powder on pumice.

The efficiency of these catalysts in amination was found to be surprisingly low, the most active being that form ethyl amine tungstate. Though each of the blue oxide of tungsten catalysts were subjected to 10 to 12 working hours of catalysts, their physical properties seemed entirely unimpaired—no carbonization being observed. The best temperature and highest yields with these catalysts are given in table IV.

TABLE IV
Alcohol and Ammonia 1:1.5 over Oxide of Tungsten

Catalyst	C	C	D	E	F
Alcohol	Butyl	Butyl	Butyl	Butyl	Ethyl
Rate	8	5.7	5.2	5.2	5.8
Temp.	365°	365°	320°	365°	400°
% Amines	2.98	1.55	3.43	6.22	7.73

The gases evolved were collected and analyzed with catalyst E at 365° with the following results:

Temp.	Total gas	C_4H_8	H_2	% C_4H_8	% Nitrile
365°	23.3	19.4	3.9	26.8	2.69
365°	20.8	17.8	3.0	25.3	2.18

from which it appears that the blue oxide of tungsten is a decided dehydration catalyst—agreeing well with the findings of Sabatier and Mailhe¹.

Other Catalysts

Catalyst G consisted of 20 g. of alumina precipitated on pumice from sodium aluminate by sulphuric acid. It became heavily carbonized in a single run with butyl alcohol and ammonia.

Catalyst H was prepared similarly to B using 25 g. zirconium nitrate on pumice. It carbonized badly in a single run.

Catalyst I was 30 g. of a laboratory sample of silica gel which had been kept for about a year in contact with the air. After a run with butyl alcohol it was considerably discolored, amber to dark brown, but showed no surface deposits.

Catalyst J² was 30 g. of silica gel impregnated with a small percentage of thoria. It showed only slight discoloration in one run.

Catalyst K² was 30 g. of silica gel impregnated with nickel oxide which was reduced by the alcohol. It proved to be an active dehydrogenation catalyst producing much nitrile. It discolored about as I.

The performances of these catalysts can be seen in the following Table, V, which gives the optimum temperatures and percent of amines formed.

¹ Ann. chim. phys. [8] 20, 328 (1910).

² For catalysts J and K we are indebted to Dr. E. H. Barclay of this laboratory.

TABLE V
Butyl Alcohol and Ammonia, 1:1.5

Catalyst	G	H	I	J	K
Rate	5.6	5.75	5.58	5.75	5.8
Temp.	380°	360°	390°	360°	350°
% Amines	6.55	15.0	4.60	16.4	9.63

At 350° and at 405° with catalyst K analysis showed 24.7 and 40.1% of nitrile on the alcohol used.

Silica Gel

Our gel was prepared¹ by adding, with vigorous stirring, a sodium silicate solution (4.5% Na₂O) to an equal volume of 10% pure hydrochloric acid. After the gel sets, it is broken into large fragments which are placed in a tray having a bottom of wire netting and suspended in running water for several days. The gel is dried at temperatures rising by stages to 180° before being placed in the catalyst tube.

For charging the reaction tube 30 g. of the gel in fragments 0.5 to 0.7 cm. were required. After running for 25 hours with butyl alcohol and ammonia there was no diminution in the activity of this catalyst. All of the runs in the following Table VI were made with the same sample² of catalyst, the runs are numbered in the order in which they were made.

TABLE VI
Alcohols with Ammonia 1:1.5, Special Silica Gel

Run	3	2	4	5	1
Alcohol	Methyl	Ethyl	Ethyl	Propyl	Butyl
Rate	5.9	5.6	5.6	6.2	5.5
Temp.	Percent		Amines		Formed
300°	—	—	—	—	3.7
320°	5.4	5.1	5.6	14.6	5.4
340°	8.4	9.5	8.9	19.8	6.5
360°	12.4	12.7	12.1	24.1	8.1
380°	17.0	18.5	19.9	26.4	11.7
400°	23.3	25.6	25.6	29.6	18.3
420°	31.0	31.1	30.8	32.4	20.7
430°	—	—	—	—	20.4

Propyl alcohol appears to be most readily aminated. About 400°-420° is the best temperature.

The run of butyl alcohol was continued for 3 hours using 0.56 mole of the alcohol. The lower layer of the product weighed 8.59 g. and contained 0.0034 moles of amines while the top layer weighed 24.78 g. with 0.11 moles of amines or 20.3%. A new run was made with the same gel and samples taken at intervals with the following results: after 1 h. 22.8%, after 6 h. 23.2%. After standing cold over night it was started again and gave: after 1 h. 22.4%, after 3 h. 20.7% and after 6 h. 22.9% amination.

¹ Method in use in this laboratory due to Dr. Patrick.

² Kindness of Dr. E. H. Barelay of this laboratory.

The gases evolved were studied and found as follows:

TABLE VII

Temp.	Alcohol	Gas per min.	C_nH_{2n} c.c.	H_2 c.c.	C_nH_{2n} %	H_2 %
400	Ethyl	7.77	3.28	4.48	4.72	3.22
415	Butyl	8.90	6.75	2.15	10.90	1.75 (fresh gel)
415	Butyl	12.85	7.85	5.00	12.80	4.06 (long used gel)

From these figures it appears that silica gel dehydrates moderately well but dehydrogenates much less than thoria, which is a great advantage in this reaction.

More extensive runs and complete analyses on methyl, ethyl, n-propyl and n-butyl alcohols using fresh samples of gel in each case gave the results of Table VIII.

TABLE VIII

Alkylation of Ammonia by Various Alcohols over Silica Gel.

1 Mole Alcohol to 1.5 Ammonia in 6 hours.

Alcohol	Temp.	Total	Percent Amines			% Alkylation
			Prim.	Sec.	Tert.	
Methyl	328°	4.9	—	—	—	—
	360°	9.0	—	—	—	—
	395°	16.1	—	—	—	—
	423°	25.7	5.9	17.6	2.2	47.7
	447°	29.8	—	—	—	—
	481°	34.1	14.3	17.9	1.9	55.8
	510°	32.8	—	—	—	—
Ethyl	354°	4.9	—	—	—	—
	395°	10.6	—	—	—	—
	415°	15.5	4.3	7.4	3.8	30.6
	436°	19.2	—	—	—	—
	456°	21.5	7.8	9.7	4.1	39.4
	477°	22.2	—	—	—	—
	500°	17.3	—	—	—	—
Propyl	520°	14.2	—	—	—	—
	300°	8.0	—	—	—	—
	331°	12.7	—	—	—	—
	359°	18.7	7.6	10.3	0.76	30.6
	388°	27.8	—	—	—	—
	420°	32.9	10.5	10.8	2.6	48.8
	448°	19.5	15.1	3.0	1.4	25.4
Butyl	468°	9.0	—	—	—	—
	490°	3.1	—	—	—	—
	381°	10.5	0.45	9.6	0.53	21.4
	407°	15.3	7.4	7.1	0.81	24.0
	430°	17.4	10.9	5.4	1.14	25.0
	472°	12.7	8.4	2.9	1.45	18.6

A different preparation of gel showed with butyl alcohol a similar maximum yield but a sharper break in the temperature-yield curve, under similar conditions, as Table IX indicates.

TABLE IX
System BuOH-NH₃

Temp.	320°	354°	381°	396°	420°	452°	472°	493°
% Amines	3.29	4.77	9.40	10.90	14.44	17.40	6.60	2.86

A silica gel for general commercial catalytic and adsorption purposes prepared by the Davison Chemical Company of Baltimore was tested on ethyl alcohol for comparison purposes. Taste revealed the presence of sodium sulphate in this gel but the quantity present was not determined. Thirty-five grams of the gel in fragments of about 0.3 cm. diameter were used as a catalyst charge. The results obtained with ethyl alcohol and ammonia (Molal ratio 1:1.5 at a flow rate of one mole EtOH per 5.6 hrs.) are given in Table X,

TABLE X

Temp.	354°	375°	402°	426°	454°	481°
% Amines	5.28	6.80	9.47	10.21	9.44	9.54

whereby it is seen that its efficiency falls far short of that of the active silica gel prepared in the laboratory.

Summary

The alkylation of ammonia by methyl, ethyl, n-propyl, and n-butyl alcohols, by passing their vapors with ammonia over catalysts at 300-500°, has been studied quantitatively. The following catalysts, arranged in the order of ascending effectiveness, have been studied: blue oxide of tungsten, com'l silica gel, alumina, silica gel impregnated with nickel oxide, zirconia, silica gel impregnated with thorium, and special silica gel.

For high activity, long life, and absence of side reactions, the special silica gel has been found to be much the best. The optimum temperatures, percentages of alcohol converted to amines, and the ratios of primary, secondary, and tertiary amines formed are as follows: methyl, 480°, 56%, 5:12:3; ethyl, 465°, 39.5%, 2:5:3; n-propyl, 415°, 49%, 10:11:8; n-butyl, 430°, 25%, 11:11:3.

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BIOGRAPHY

The author of this dissertation was born at Charleston, S. C., July 17, 1899. He received his early education in the private and public schools of the same city and at the Porter Military Academy of Charleston, from which he was graduated in June 1915. He received the degree of Bachelor of Arts from the College of Charleston in May 1918. In the fall of the same year he entered the Graduate Department of Chemistry of the Johns Hopkins University, majoring in Chemistry with Physical Chemistry and Mathematics as subordinate subjects. He held Hopkins Scholarships for the years 1918-19, 1919-20, 1920-21, and the Du Pont Fellowship for 1921-22.

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